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Optical Brighteners: Movement and Degradation in Paper

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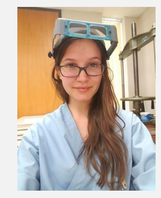

Introduction

This poster investigates the potential discoloration and deterioration of optical brightening agents (OBAs) within paper. Specifically, this poster looks at the introduction of OBAs into non-OBA containing paper and observing how they degrade after being placed within a climate chamber. This experiment was inspired by a previous treatment; while attempting the removal of a gummed tape from an intaglio paper, water was used to remove the water-soluble adhesive tape. It was not realized until after the treatment that the tape's paper carrier contained optical brightening agents and that these brighteners had reacted with the application of water, creating tidelines within the print that were only visible in UV fluorescence.

What Are Optical Brighteners?

Optical Brightening Agents (OBAs) – also known as optical brighteners, fluorescent whitening agents (FWAs), or fluorescent brightening agents (FBAs) – have been used in paper production since the 1950s.[1] Originally used to brighten textiles, today they are an ever-present part of our surroundings and can be found in textiles, clothing detergents, paper, and plastic materials. There are thousands of types of optical brighteners, but the vast majority are derivatives of the chemical stilbene (*Fig. 2*).[2] OBAs work by absorbing light within the UV range and emitting it within the violet-blue range of visible light. When viewed under UV range between 350 nm - 395 nm, OBAs in paper typically show a blue colored fluorescence. While it varies depending on the optical brightener, OBAs typically have an absorption peak at around 375 nm and an emission peak around 450 nm.[3] This fluorescence in the blue spectra of visible light acts to visually combat against gradual yellowing within these materials. OBAs are water soluble and therefore susceptible to movement when exposed to water or other solvents. OBAs are also not lightfast, are sensitive to bleaching materials, and their fluorescence can be reduced when exposed to acidic conditions. Over time, OBAs within paper deteriorate in three steps: First, the quenching of the optical brightener, where it can no longer function and emit light. Second, the darkening and yellowing of the optical brightener itself. Third, the subsequent damage to the substrate caused by the degraded optical brightener. [4]

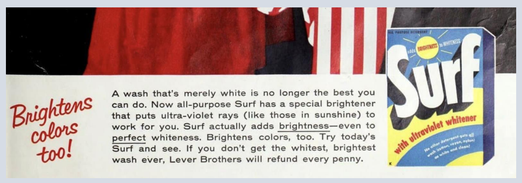
Brightens colors too!
A wash that's merely white is no longer the best you can do. Now all-purpose Surf has a special brightener that puts ultra-violet rays (like those in sunshine) to work for you. Surf actually adds brightness—even to perfect whiteness. Brightens colors, too. Try today's Surf and see. If you don't get the whitest, brightest wash ever, Lever Brothers will refund every penny.
Surf
with ultraviolet whitener

Fig. 1 Surf detergent ad, 1957, "all-purpose surf has a special brightener that puts ultra-violet rays…to work for you"

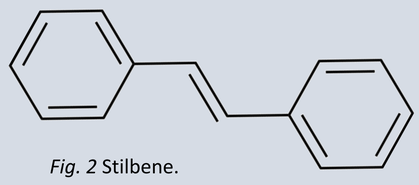

Fig. 2 Stilbene.

Methodology

This research intends to imitate the circumstances of the previous treatment by:

- Creating paper samples with tape carriers, both containing OBAs and without
- Local aqueous treatment with water
- Artificially aging the samples

Materials

Papers Used	Gummed Tapes Used
Blotter: Klug Conservation, sold as Blotter Board at a thickness of 2mm and grammage of 700 Arches Rives BFK: item number A1795173, has a 250 grammage, is made from cotton fibers, and does not contain any optical brighteners Hahnemühle, copperplate: 350 g/m², listed as acid free and age resistant.	Klug Conservation: gummed tape made with a potato-starch based adhesive. The tape carrier is made of 100% bleached cellulose with a pH of 7.0 and contains no OBAs Clairefontaine: 60g white paper gummed tape, containing no OBAs Office paper: contains optical brighteners; used as a substitute as no gummed tape with OBAs could be found

Sample Creation

Papers were cut into 10x10 cm square samples. For the gummed tape samples, the tape (7 cm strip) was applied to one edge of the paper, folding around the edge (*Fig. 3*). For the strip of office paper containing OBAs, a strip (2 x 7 cm) was simply placed on the substrate when it came time for treatment.

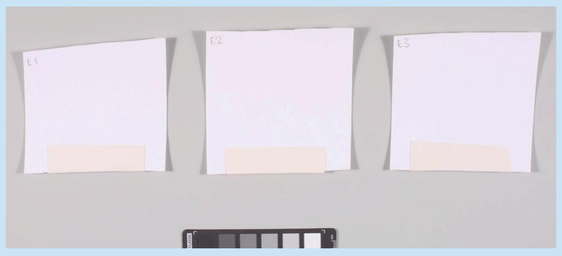

Fig. 3 Gummed tape samples before 'treatment'

'Treatment'

Water was applied to the samples using a pipette so that the amount of water added to each sample could be measured. Gummed tape samples were removed with both mechanical action and with water. For the office paper samples, strips of office paper were placed near the edge of the paper samples and 1 ml water was applied to them and left to dry. Additional paper samples, without tapes, were treated with water to serve as a comparison to the tape samples.

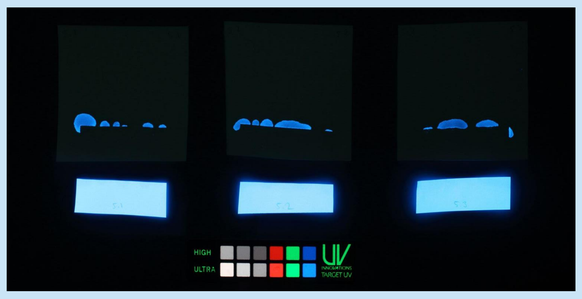

Fig 4 UV light. OBA samples, post 'treatment' and before aging, showing the migration of optical brighteners into the paper samples.

Aging

Post treatment, samples were cut in half. One half was subjected to artificial aging while the other half was saved for later comparison. The now 5 x 10 cm samples were placed in a climate chamber set at 80°C 65% RH for six days.

Fig. 5 Samples in the climate chamber.

Results

A Misleading Start

It was initially thought that the discoloration of OBAs was much more prevalent when first looking at the samples in visible light. What was initially thought to be the deterioration of OBAs was instead identified as discoloration due to local application of water. The Arches Rives BFK samples with OBAs (*Fig. 6)* show some visible darkening where the OBAs are present. However, the water-only intaglio paper samples show a similar discoloration (*Fig. 7*). For this reason, the discoloration seen in *Figure 6* cannot be confidently linked to the degradation of OBAs.

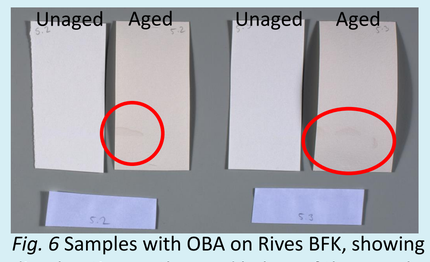

Fig. 6 Samples with OBA on Rives BFK, showing discoloration on the aged halves of the samples.

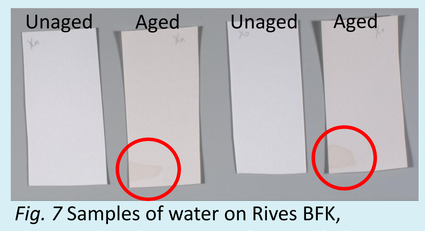

Fig. 7 Samples of water on Rives BFK, showing discoloration on the aged halves.

First State of Degradation

The first stage of deterioration for optical brighteners is the quenching of the optical brighteners over time, which can be seen as a decrease in fluorescence under UV. This stage can be seen when comparing the aged and unaged samples of both intaglio papers (*Fig. 8*).

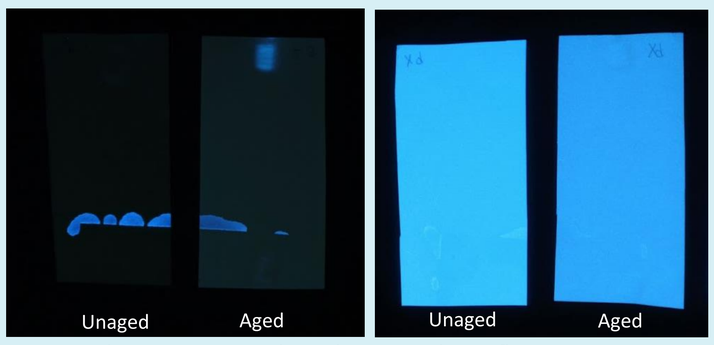

Fig. 8a Arches Rives BFK samples with OBAs, under UV fluorescence, 2 second exposure. *Fig. 8b* Hahnemühle Copperplate with OBAs, under UV fluorescence, 2 second exposure. Note that the fluorescent areas in the aged sample appear less bright than those seen in the unaged sample.

Second State of Degradation

The second stage of deterioration for optical brighteners is the darkening and yellowing of the OBAs. Thought the second stage is more difficult to spot, there is one sample which could show an example of the darkening of OBAs after aging, seen in one of the blotter samples. The appearance of OBAs in the blotter samples look different from the intaglio papers due to the paper's absorption rate. The blotter samples have concentrated points of OBAs and visible tidelines surrounding these areas. These small areas with a high concentration of optical brighteners give the best opportunity to visibly see if the OBAs are darkening due to degradation. The samples in *Figure 9* does show a small area of darkening, exactly where some optical brighteners sit when viewed under UV fluorescence.

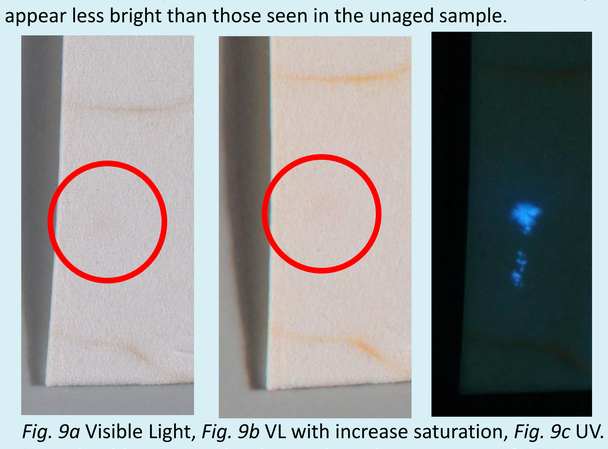

Fig. 9a Visible Light, *Fig. 9b* VL with increase saturation, *Fig. 9c* UV. Note that blotter samples do not show the same type of OBA placement seen in both intaglio paper samples (*Fig.8)*. This is due to the absorption rate of the blotter compared to the other papers.

Conclusion

The initial questions asked at the beginning of this research were: What are the consequences of this local movement of optical brighteners into a paper without OBAs? Will they cause discoloration in the future?

- Evidence suggests that some deterioration of OBAs is possible over time. However, these results were caused by non-museum conditions and did not provide enough time to create significant discoloration of the OBAs.
- Clear discoloration from the application of water during local treatment did appear within the same amount of time. While not the focus of this paper, the sample set acts as a warning of the potential discoloration caused by local treatment in the formation of tidelines and dark stains.

An Unexpected Result: Migration of Optical Brighteners from Plastics

Noticeable in several samples is the unexpected addition of fluorescence caused by the plastic clips used to hold the samples in place while they sat in the aging chamber (*Fig. 10*). The clips which caused this fluorescence had been recently purchased at the time of use but had been mixed with the collection of older clips (*Fig. 11*). Only the samples that had been attached with the new clips showed the blue fluorescence (*Fig. 12*). Unfortunately, the author was unable to find the source of these clips.

Some literature does note that OBAs can migrate from the plastics into physically contacted materials.[5] One article mentions that optical brightener bis-benzoxazolyl-stilbene is insoluble in plasticizers, making it incompatible with flexible polyvinylchloride (PVC) and polyethylenes, resulting in the OBA migrating to the surface of the plastic.[6] It could be possible that a similar phenomenon is occurring here with the additional condition that the clips and paper were in contact in a high temperature and high humidity environment.

Fig 10, 11, 12 Top Left: samples in the climate chamber. Bottom Left: New and old clips used, note the difference in coloration. Above: UV light, areas where OBAs migrated from the clips to the paper.

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[3] Messier, Paul, Valerie Baas, Diane Tafilowski & Lauren Varga. "Notes on dating photographic paper." *Topics in Photograph Preservation*, Vol. 11. (January 2005): 123-130.

[5] M. Gandhimathi, K. Murugavel, and Ravi T.K. "Migration study of optical brighteners from polymer packing materials to jam squeeze and fruit drink by spectrofluorimetry and RP-HPLC methods." *J Food Sci Technol,* Vol. 51 (June 2014): 1133-1139.

[6] Jervis, Daniel A. "Optical brighteners: Improving the colour of plastics." *Plastic Additives & Compounding* (November/December 2003): 42-46.

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